COMBUSTION CHARACTERISTICS OF MILD-GASIFICATION CHARS

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INTRODUCTION

The commercial success of mild coal gasification (MG) depends on economical utilization of the byproduct char. While various utilization options are being considered (e.g., coke manufacture, activated carbon production, and further gasification), the boiler fuel market is likely to be the largest potential consumer. A key concern is the combustion performance of MG chars relative to more conventional boiler fuels. This paper summarizes recent results of MG char characterizations conducted by Oak Ridge National Laboratory (ORNL) for Morgantown Energy Technology Center (METC) of the Department of Energy (DOE). The char characterizations are being conducted in conjunction with MG liquid characterizations.

EXPERIMENTAL METHODS AND MATERIALS

Char and Reference Fuel Samples

Char samples were obtained from two MG processes, one developed by the United Coal Company (UCC) and the other by SGI International (SGI). A single UCC char sample was obtained from a typical test on the UCC MG test unit [test run P1/12; United Coal Company (1988)]. In this case, the parent coal was Kentucky Williamson No. 2 seam, a high-volatile, bituminous coal. Three SGI char samples were obtained, each representing successively higher devolatilizations of Montana Rosebud subbituminous coal. These samples were produced in cooperative tests between SGI and Peabody Coal Company [Estergar(October 1988)]. Four widely-used reference fuels were also included to extend the applicability of the results: Texas lignite; Kentucky No. 9 high-volatile, bituminous; delayed petroleum coke, and anthracite.

Table 1 summarizes proximate, ultimate, and BET analyses of the char samples, typical analyses of the parent coals, and reference fuel analyses. It is clear that all the SGI chars have more volatiles and much greater surface area than the UCC char. Such differences are believed to be due both to the parent coals and to higher temperature and residence time in the UCC process.

Thermogravimetric Tests

Low-temperature combustion tests were conducted for each char and reference fuel using a Netsch model STA 429 thermogravimetric (TG) analyzer. Previous studies [e.g., Jenkins et al (1973),

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Ceely and Daman (1981), Khan (1987)] have demonstrated the usefulness of TG comparisons of coals and chars. Standard operating procedure involved heating approximately 20 mg of 105-125 μm particles from ambient up to 1273 K. Heating rate was 10 K/min, and gas flow was 190 cc/min. Dry air (21% oxygen) was injected directly into the sample crucible. Sample weight, rate of weight change, and temperature were continously monitored.

The limiting external oxygen mass-transfer rates for similar conditions have been determined previously [Daw and Mitchell (1986)]. These limits were reevaluated during the current tests based on the observed burning rates for previously tested reference fuels and on the asymptotic high-temperature burning rates of the chars [see Mulcahy and Smith (1969)]. Measured burning rates were corrected to true intraparticle rates by the relationship of Young and Smith (1981):

$$RI = R/[1 - (R/RMT)]^n \qquad (1)$$

where RI is the internally-limited burning rate (i.e., the rate limited solely by intraparticle processes), RMT is the maximum rate possible due to external mass transfer of oxygen, R is the observed burning rate, and n is the effective reaction order in oxygen. In most cases such corrections were small.

Fixed-Bed Reactor Tests

Higher-temperature combustion tests were conducted using the fixed-bed reactor at Babcock and Wilcox's (B&W) Alliance Research Center. This reactor was constructed for the Atmospheric Fluidized Bed Combustion Fuels Characterization Program sponsored by the Electric Power Research Institute (EPRI). B&W has used this reactor to characterize a range of coals, refuse derived fuels, and coal-cleaning refuse for EPRI and Consolidated Edison Company of New York [Chandran et al(1988, 1989)]. Described in detail elsewhere [Chandran et al (1987)], the reactor is a 5.1-cm diameter quartz vessel containing a bed of spent fluidized bed combustor sorbent. The bed is heated electrically, and preheated nitrogen/oxygen mixtures enter the top, flowing down through the bed. Fuel particles are injected batchwise via a solenoid valve, and they land on top of the bed where they devolatilize and burn. The reactor is designed for gas velocities, temperatures, gas compositions, and particle sizes similar to those expected for AFBC. The operating ranges for each of the fuels in this study were: 1045-1215 K gas temperature, 3-10 volume % oxygen, 1.5-1.6 atm total pressure, and 1.3-1.5 m/s superficial gas velocity.

Fuel particles were prescreened into two narrow fractions: 1) 105-125 μm (115 μm mean) and 2) 500-595 μm (547 μm mean). The fuel batch weight was chosen such that the reactor oxygen concentration decreased by less than 10% at the maximum combustion rate. Devolatilization and combustion were monitored by continnous analysis of the reactor exit gas for carbon dioxide, carbon monoxide, and hydro-carbons. Net carbon loss-vs.-time was determined by integrating total gas carbon concentration. Particle temperatures were estimated by heat balances accounting for conduction, convection, radiation, and heat of combustion.

EXPERIMENTAL RESULTS AND DISCUSSION

Thermogravimetric Results

Figures 1 and 2 illustrate the observed variation in the rate-vs-temperature profiles for the reference fuels. From these plots it is clear that the UCC char ignites and burns more slowly than all three SGI chars at the conditions tested. Many different ignitability/reactivity measures can be derived from TG profiles. Table 2 lists some example measures to illustrate comparisons of the fuels tested here. While minor variations occur depending on the measure used, the general trends are readily apparent: 1) Texas lignite is by far the most ignitable and reactive; 2) the SGI chars and Kentucky 9 bituminous are similar and slightly less ignitable and reactive than lignite; 3) the UCC char and petroleum coke are similar and significantly less ignitable and reactive than the SGI chars and Kentucky 9; and 4) anthracite is by far the most difficult to burn.

Fixed-Bed Reactor Results

Figure 3 compares the fixed-bed profiles for 115 μm particles of each fuel exposed to 3% oxygen at 1100-1120 K. As with the TG results, the fixed-bed profiles clearly distinguish among the fuels. Texas lignite burns by far the most rapidly, followed closely by Kentucky No. 9 bituminous and the SGI chars. Petroleum coke, UCC char, and anthracite are again much slower. Quantitative comparisons can be made using various profile measurements such as: 1) burning rate at char ignition, 2) degree of fixed carbon conversion after a fixed elapsed time, and 3) time to achieve a given fixed-carbon conversion. For the fuels tested the basic profile shapes following char ignition are similar, and thus all three of the above measures give identical rankings. Measurement 1 above, the burning rate at char ignition, is selected as the key index for further discussion.

Table 3 compares the estimated initial char burning rates for the profiles in Figure 3. The fuel ranking resulting from these burning rates is virtually identical with the rankings developed from burning rates evaluated at other fixed-bed conditions. An important point emerging from these comparisons is that the relative fuel reactivities are consistent over the range of fixed-bed and TG conditions tested.

Combined Burning-Rate Expressions

Estimates of the true intra-particle combustion rate at char ignition, RI, were made for each fuel and test condition (both TG and fixed-bed) using Eqn. 1. As expected, the corrected rates were found to follow the standard Arrhenius rate expression:

$$RI = A \exp(-E/Rg\ Tp)\ PO2^n = kw\ PO2^n \qquad (2)$$

where A is the pre-exponential rate coefficient, E is the effective activation energy, Rg is the ideal gas constant, Tp is particle temperature, PO2 is bulk-gasoxygen partial pressure, and

kw, was determined assuming n to be 0.5. Within the scope of this study it is not possible to select with certainty any value of n between 0.5 and 1. Essenhigh(1981) has shown that Zone 2 combustion (combustion in which pore diffusion is a significant controlling factor) should exhibit an effective reaction order of 0.5. As discussed below, the Arrhenius fits of the present data suggest Zone 2 burning. Selection of n=0.5 is also consistent with earlier fixed-bed data [Daw (1988)] and conforms more closely to the comprehensive study by Suuberg et al (1988).

Figure 4 depicts the combined Arrhenius fits for the chars and reference fuels (note: the horizontal axis is the reciprocal of estimated particle temperature not gas temperature). Comparing slopes, the activation energies for all four chars do not seem to differ greatly. Table 4 summarizes the Arrhenius parameters quantitatively. Within experimental uncertainty, all the activation energies fall within the 4.8 to 9.6 kJ/mole (20 to 40 kcal/mole) expected for Zone 2 burning [Essenhigh (1981)]. Thus the assumption of 0.5 oxygen reaction order is reasonable.

CONCLUSION

The above results suggest that the bituminous char tested is more suitable for firing in non-sensitive applications, such as fluidized beds, stokers, or U-flame boilers. The subbituminous chars evaluated may be sufficiently reactive for pulverized firing in bituminous boilers with little or no supplemental fuel.

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Table 1. Ultimate and proximate analyses of the test chars, parent coals, and reference fuels.

Ultimate*

Chars:	C	H	N	Cl	Tot. S	Pyr. S	Sul. S	Org. S
UCC	83.88	3.18	1.46	0.077	0.70	0.036	0.0061	0.66
SGI 4	63.40	3.07	1.00	0.0037	0.78	0.055	0.053	0.67
SGI 20	68.31	2.34	1.13	0.0009	0.99	0.016	0.0094	0.96
SGI 48	66.50	3.27	1.12	0.0022	0.64	0.16	0.021	0.46
Parent Coals:								
KY WIL. 2 (UCC)	78.18	5.24	1.46	0.13	0.98	-	-	-
MT ROS. (SGI)	54.82	3.72	0.79	0.02	0.63	0.33	0.040	0.42
Ref. Fuels:								
TX LIG.	33.27	3.28	0.77	-	0.75	-	-	-
KY 9	65.82	4.72	1.40	-	3.48	-	-	-
PET. CK.	85.75	3.87	1.46	-	5.18	-	-	-
ANTH.	79.80	1.79	0.78	-	0.53	-	-	-

Proximate*

Chars:	WATER	ASH	VM	FC	BET+
UCC	2.32	5.86	11.49	80.33	0.197
SGI 4	10.82	15.27	18.34	55.57	22.6
SGI 20	6.84	15.63	13.99	63.54	30.5
SGI 48	8.61	11.52	23.72	56.15	11.2
Parent Coals:					
KY WIL. 2	1.80	5.00	33.80	59.40	-
MT ROS.	19.84	9.16	39.02	51.82	-
Ref. Fuels:					
TX LIG.	33.27	7.25	30.58	28.90	-
KY 9	6.78	10.81	37.75	44.66	-
PET. CK.	1.10	2.14	13.86	82.90	0.230
ANTH.	4.23	10.85	5.74	79.18	-

* All analyses as weight percent on an as-received basis (i.e., moisture and ash included).
+ BET surface area by N_2 adsorption (m^2/g).

Table 2. Example measures of TG reactivity for the fuels tested.

Fuel	Tign	Rign	Tmax	FCCl	FCCh	T50
UCC	753	7.2×10^{-4}	847	0.10	0.50	823
SGI 4	723	9.6×10^{-4}	753	0.39	0.71	785
SGI 20	703	5.9×10^{-4}	801	0.33	0.71	793
SGI 48	713	1.3×10^{-3}	778	0.45	0.84	781
TX LIG.	668	2.6×10^{-3}	681	0.84	0.91	703
KY 9	748	1.9×10^{-3}	798	0.28	0.59	798
PET. COKE	761	7.8×10^{-4}	823	0.0	0.36	838
ANTHRACITE	793	2.7×10^{-4}	918	0.0	0.05	883

Tign = char ignition temperature (K) ; Rign = rate at char ignition (g/g s) or (1/s); Tmax = maximum burning rate temperature (K); FCCl = fractional fixed carbon conversion at 773 K; FCCh = fractional fixed carbon conversion at 823 K; T50 = temperature at which fixed carbon conversion reaches 0.5 (K)

Table 3. Typical fixed-bed combustion results for 115 micron particles in 3% oxygen at 1100-1120 K.

Fuel	Tg	Vo	Tp	Rign
UCC	1120	1.51	1127	0.059
SGI 4	1120	1.48	1174	0.30
SGI 20	1114	1.69	1164	0.36
SGI 48	1120	1.45	1183	0.47
TX LIGNITE	1101	1.60	1189	1.5
KY 9	1103	1.59	1141	0.59
PET. COKE	1116	1.67	1132	0.090
ANTHRACITE	1114	1.46	1117	0.024

Tg = gas temperature (K) ; Vo = superficial gas velocity (m/s) ; Tp = estimated particle temperature (K); Rign = burning rate (1/s)

Table 4. Arrhenius char combustion parameters derived from the combined combustion data.

Fuel	A*	E+	r^2
UCC	1.7×10^{4}	5.71 ± 0.57	0.990
SGI 4	7.2×10^{5}	6.70 ± 0.57	0.997
SGI 20	3.0×10^{4}	7.00 ± 0.88	0.994
SGI 48	4.9×10^{4}	5.61 ± 0.53	0.997
TX LIGNITE	1.8×10^{5}	5.38 ± 0.31	0.999
KENTUCKY 9	1.6×10^{6}	7.05 ± 0.91	0.996
PET. COKE	2.0×10^{4}	5.73 ± 0.55	0.990
ANTHRACITE	2.8×10^{4}	6.47 ± 1.15	0.974

A = Arrhenius pre-exponential factor (s^{-1} $atm^{-0.5}$);
E_2 = activation energy (kJ/mole) and 95% confidence interval;
r^2 = coefficient of determination for regression

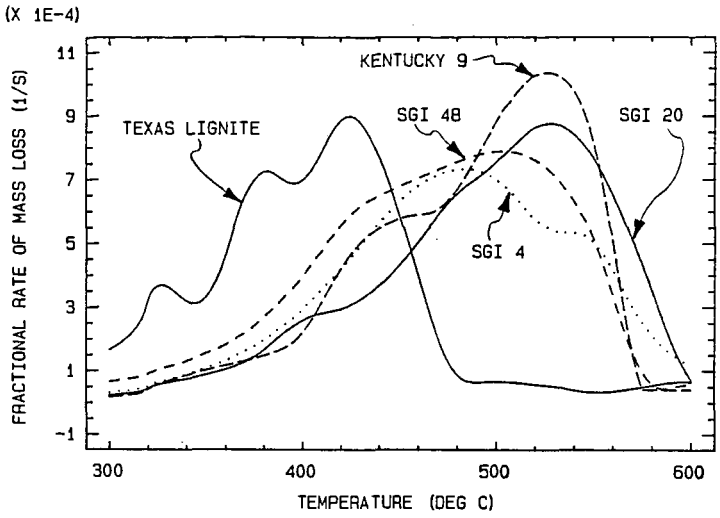

Figure 1. TG rate profiles for the more reactive fuels.

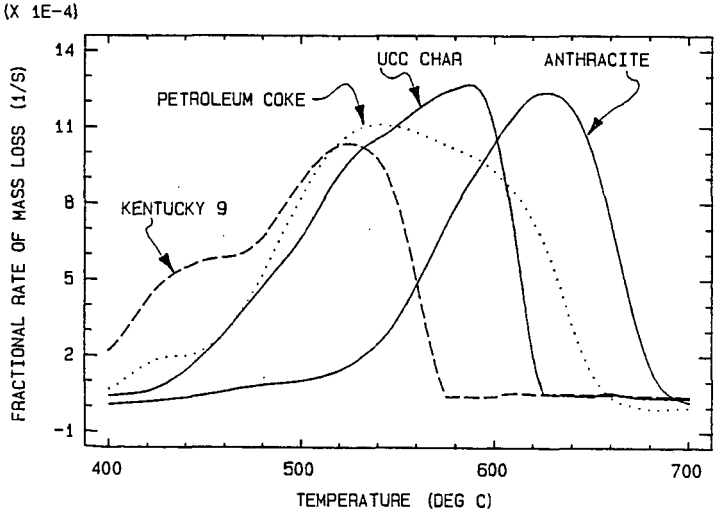

Figure 2. TG rate profiles for the less reactive fuels.

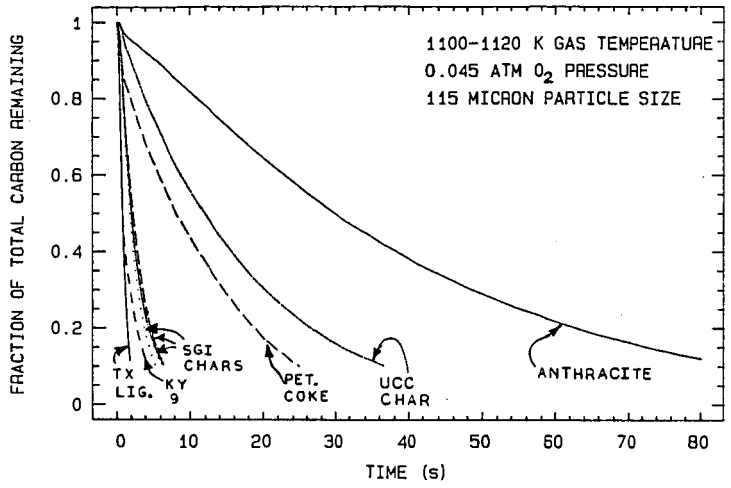

Figure 3. Comparison of the fixed-bed profiles for all the fuels at one test condition.

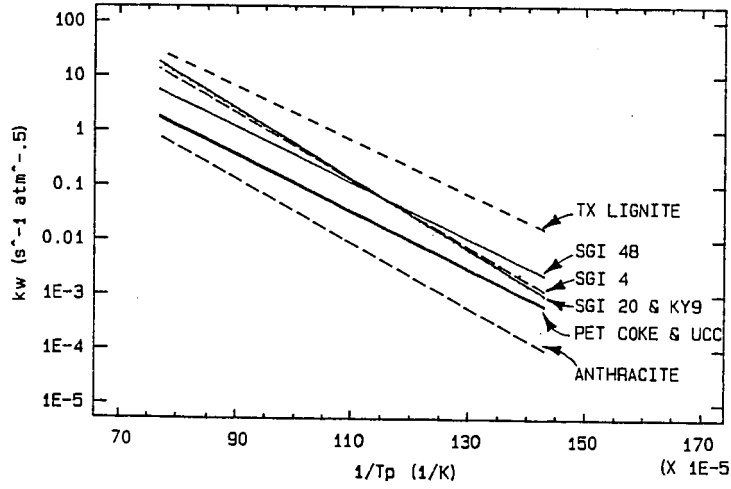

Figure 4. Comparison of Arrhenius plots for all the fuels tested.